Final Technical Report

Grant #: FA9550-07-1-0345

Grant Title: High-pressure CVD growth of InN and indium-rich group III-nitride compound semiconductors for novel mid- and far-infrared detectors and emitters

Reporting Period: April 01, 2007 to 30 November 2009

Nikolaus Dietz, PI

Department of Physics and Astronomy

Georgia State University (GSU)

Atlanta, Georgia 30303

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: Yes
Prior: Donald J. Silversmith, Electronic and Photonic Materials, Physics and Electronics Directorate(NE)

Extensions granted or milestones slipped, if any: None

Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none): YES

Abstract (200 words)

During the grant period, the growth and optimization of InN and indium-rich $In_{1-x}Ga_xN$ layers grown by high-pressure CVD was explored at rector pressures up to 20 bar and at growth temperatures of 700°C - 900°C. The main emphasis was to evaluate the reactor pressure and growth temperature relation at which epitaxial InN and indium-rich $In_{1-x}Ga_xN$ layers can be stabilized. The results showed that for reactor pressures around 15bar, the potential InN growth temperatures is around 850°C, which is more than 200°C higher compared to low-pressure MOCVD. The growth at higher pressures (above 15 bar) was not successful due to carrier gas contamination problems caused in gas compression stage, an issue that has to be addressed in the next phase of the research program.

The structural, electrical and optical properties of InN and indium-rich $In_{1-x}Ga_xN$ layers grown on Sapphire and GaN/Sapphire templates have been studied by x-ray diffraction, Raman, infrared reflectance and transmission spectroscopy. The results obtained from Raman and IR reflectance measurements showed that single phase $In_{1-x}Ga_xN$ layers with $(0.2 < x < 0.5)$ can be obtained. However, for higher gallium concentrations the FWHM values in the XRD Bragg reflexes become significant broader, indicating that further process improvements are needed.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **AUG 2012**	2. REPORT TYPE	3. DATES COVERED **01-04-2007 to 30-10-2009**

4. TITLE AND SUBTITLE
High-pressure CVD Growth Of InN and Indium-rich Group III-nitride Compound Semiconductors For Novel Mid-and Far-infrared Detectors And Emitters

5a. CONTRACT NUMBER
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Georgia State University,Department of Physics and Astronomy,Atlanta,GA,30303

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**25**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
01-02-2010	Final Technical Report	01-04-2007 - 30-11-2009

4. TITLE AND SUBTITLE	
High-pressure CVD growth of InN and indium-rich group III-nitride compound semiconductors for novel mid- and far-infrared detectors and emitters	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER FA9550-07-1-0345
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Nikolaus Dietz	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	**8. PERFORMING ORGANIZATION REPORT NUMBER**
Georgia State University Department of Physics & Astronomy, 400 Science Annex Atlanta, GA 30303	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	**10. SPONSOR/MONITOR'S ACRONYM(S)**
Dr. Kitt Reinhardt, Ph.D. Program Manager, AFOSR/RSE 875 N. Randolph Street, Suite 325, Room 3112 Arlington, VA 22203-1768 kitt.reinhardt@afosr.af.mil	AFOSR/NE
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

13. SUPPLEMENTARY NOTES

14. ABSTRACT

During the grant period, the growth and optimization of InN and indium-rich In1-xGaxN layers grown by HPCVD was explored at rector pressures up to 20 bar and at growth temperatures of 700°C - 900°C. The main emphasis was to evaluate the reactor pressure and growth temperature relation at which epitaxial InN and indium-rich In1-xGaxN layers can be stabilized. The results showed that for reactor pressures around 15bar, the potential InN growth temperatures is around 850°C, which is more than 200°C higher compared to low-pressure MOCVD. The growth above 15 bar was not successful due to carrier gas contamination problems caused in gas compression stage, an issue that has to be addressed in the next phase of the research program. The properties of InN and indium-rich In1-xGaxN layers grown on Sapphire and GaN/Sapphire templates have been studied by x-ray diffraction, Raman, infrared reflectance and transmission spectroscopy. The results obtained from Raman and IR reflectance measurements showed that single phase In1-xGaxN layers with $(0.2 < x < 0.5)$ can be obtained. However, for higher gallium concentrations the FWHM values in the XRD Bragg reflexes become significant broader, indicating that further process improvements are needed.

15. SUBJECT TERMS

InN, InGaN, thin film growth, epitaxy, high-pressure chemical vapor deposition

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(Include area code)*

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18
Adobe Professional 7.0

Final Report on AFOSR Grant FA9550-07-1-0345

High-pressure CVD growth of InN and indium-rich group III-nitride compound semiconductors for novel mid- and far-infrared detectors and emitters

Nikolaus Dietz

Department of Physics & Astronomy, Georgia State University, Atlanta, GA 30302

Website: http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html

This final report summarizes the results of the research program NAFOSR Grant FA9550-07-1-0345, entitled "High-pressure CVD growth of InN and indium-rich group III-nitride compound semiconductors for novel mid- and far-infrared detectors and emitters." The main objectives of the research were

a) *to* fabricate and optimize InN and indium-rich $In_{1-x}Ga_xN$ alloys and heterostructures using *high-pressure chemical vapor deposition (HPCVD)* approach

b) to improve the structural properties of high quality, single-phase InN epilayers, and to reduce the free carrier concentrations in these layers to below 10^{+17} cm^{-3}, which is crucial for InN based mid to far-infrared detectors and/or THz emitters.

c) to analyze the intrinsic and extrinsic defect chemistry and their effects on the structural, electrical and optical materials properties, and

d) *to utilize real-time optical techniques to monitor and control gas phase and surface chemistry processes at elevated pressures, to assess flow kinetics and the growth of InN.*

Outline of the report

Accomplishments - Summary

As shown in the report, substantial progress has been made in the structural quality of indium-rich $In_{1-x}Ga_xN$ epilayers. The HPCVD system employed and further developed during the research project enabled the growth of indium rich $In_{1-x}Ga_xN$ layers at reactor pressures around 15 bar, and growth temperatures from 850°C - 950°C. These process conditions narrows the presently encounters growth temperature window by suppressing the decomposition of indium-rich alloys at growth temperatures required for wider band-gap group III-nitrides.

During the research program, several real-time optical diagnostics have been employed. Principal-angle-reflectance (PAR) spectroscopy has been utilized as a high surface sensitive probe, which enables to analyze the surface chemistry during nucleation and steady state growth at a sub-monolayer level. In addition, laser light scattering (LLS) was applied to characterize the surface morphology during nucleation and growth. The real-time optical monitoring techniques employed demonstrated their superiority in optimizing and controlling the growth process, as well as in gaining insight in gas phase and surface chemistry processes during HPCVD.

The growth of $In_{1-x}Ga_xN$ by HPCVD has been assessed, showing that macroscopic single phase InGaN epilayers can be achieved under optimized process conditions. Further studies are needed to improve the structural, optical and electrical properties of these epilayers. At this point, we demonstrated that the HPCVD approach allows the stabilization of highly volatile constituents/alloys such as encountered in the growth of indium-rich $In_{1-x}Ga_xN$ epilayers under process conditions not possible by MBE or low-pressure MOCVD.

Highlights:

- During the research program, two graduate students completed and received their PhD degree (see section III.2).
- The research results have been published in 9 referred publications and have been presented in 7 invited publications, 11 oral conference contributions, and 14 conference poster presentations (see section III.3).
- A provisional patent application, entitled "Improved method and apparatus for performing high pressure chemical vapor deposition" has been filed Aug. 12, 2009. This patent application describes critical design aspects of a next generation of HPCVD reactor, which integrates discoveries related to research supported during this research program.
- We showed that HPCVD enables the successful growth of high crystalline quality layers of InN on sapphire and GaN/sapphire templates. At a reactor pressure of 15 bar, the growth temperature for InN can be raised to about 850°C. Detailed studies were carried out on the precursor pulse separations and correlated to the crystalline quality of the epilayer. We also carried out extended studies on the optimum group V/III precursor ratio and its influence and the surface chemistry, crystalline quality and the reduction of the free carrier concentration in the layers. A large difference in free carrier concentrations in layers grown on GaN/sapphire templates compared to InN layers grown directly on sapphire was observed.
- The growth of indium-rich $In_{1-x}Ga_xN$ epilayers for $x<0.5$ showed that macroscopic single phase InGaN epilayers can be stabilized. At present however, the process conditions have to be adjusted of each composition region in order to stay single phase. More detailed microscopic structural analysis is needed and study potential for compositional fluctuations and understand the broadening of the XRD Bragg reflex peaks.
- In the compositional region $0.3<x<0.4$ of $In_{1-x}Ga_xN$, a significant reduction of the measured free carrier concentration is observed. The reason is not clear and further experimental studies are needed.

I. High-pressure chemical vapor deposition (HPCVD) growth of indium-rich InGaN epilayers

However, all presently employed low-pressure deposition techniques encounter significant temperature gaps in the growth of binary group III-nitrides. For instance, the optimum growth temperatures of InN and GaN differ by more than 300°C under low-pressure organometallic chemical vapor deposition growth conditions. Such a temperature gap severely limits the ternary InGaN alloy formations and their integration in wider band-gap alloys that have to be grown at higher growth temperatures. One consequence of this problem is discussed in the context of spinodal decomposition/compositional fluctuations in the ternary InGaN[1-8] system – an added problem to compositional induced lattice strain, interfacial piezoelectric polarization effects, and extended defect related effects that have to be addressed.

A potential pathway to address and overcome the difficulties associated with the phase stability, stoichiometry fluctuations and the growth temperature gap between the group III-N binaries, is to assess the pressure dependency of surface chemical reactions and growth surface stabilization, a pathway presently explored at GSU.

High-pressure chemical vapor deposition (HPCVD): Motivation and History

Research on extending OMCVD to super-atmospheric pressure is motivated by the sensitive relation between the properties of compounds and their native defect chemistry. In turn, the defects depend on the control of compound stoichiometry, that is, on the partial pressure of volatile constituents in thermal equilibrium. For many materials utilized in today's industry, the decomposition pressures are sufficiently low to permit processing at reduced pressure, which avoids fluid dynamics perturbations of process uniformity. However, there are important merging materials systems, where stoichiometry control is limited under conditions of low total pressure. For example, limitations are encountered at present in the control of the stoichiometry and defect formation for InN and indium-rich group III-nitride solid solutions in processing at reduced pressure, due to the high decomposition pressure and their vastly different partial pressures. MacChesney et al.[9] assessed within the thermodynamic limitations the growth of high-quality InN, suggesting that high pressures are needed to stabilize the compound. The calculation indicated that substantial nitrogen pressure is required to prevent thermal decomposition of bulk InN, a relationship captured by

$$p(N_2) \rightarrow p_0 \exp\left[-\frac{\Delta H_r}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \quad , \tag{1}$$

which results in the p-T^{-1} relation shown in Fig. 1[9]. This relation suggests that, for pressures $p_{N_2} \leq 10^2$ bar and substrate temperatures ≤ 900 K, the surface decomposition of InN can be effectively suppressed. Also, recent studies in the indium-gallium-nitrogen system[10] show much uncertainty in the p-T-x relations (where x stands for Ga/In ratios) due to missing experimental validation.

Even though the transition from bulk crystal growth techniques towards thin film growth techniques (e.g., MBE, MOCVD, MOVPE, CVD, etc.) opens unique off-equilibrium approaches to stabilize growth surfaces at temperatures and pressures not possible otherwise, the integration of such highly dissimilar alloys remain a main challenge due to miss-matched processing windows or stoichiometric instabilities and low dissociation temperatures that may lead to inconsistent and process dependent material properties.

Keeping this in mind, Dr. Bachmann and Dr. Banks at North Carolina State University (NCSU) addressed this problem in 1995, in a MURI research program entitled "Modeling and Control of Chemical Vapor Depositions Processes: The Control of Defects in Mixed III-V Compound Heterostructures," and started the modeling and design of reactor systems, suitable to operate at elevated pressures,[11-15], an effort which was funded by AFOSR under DOD-MURI F49620-95-1-0447.

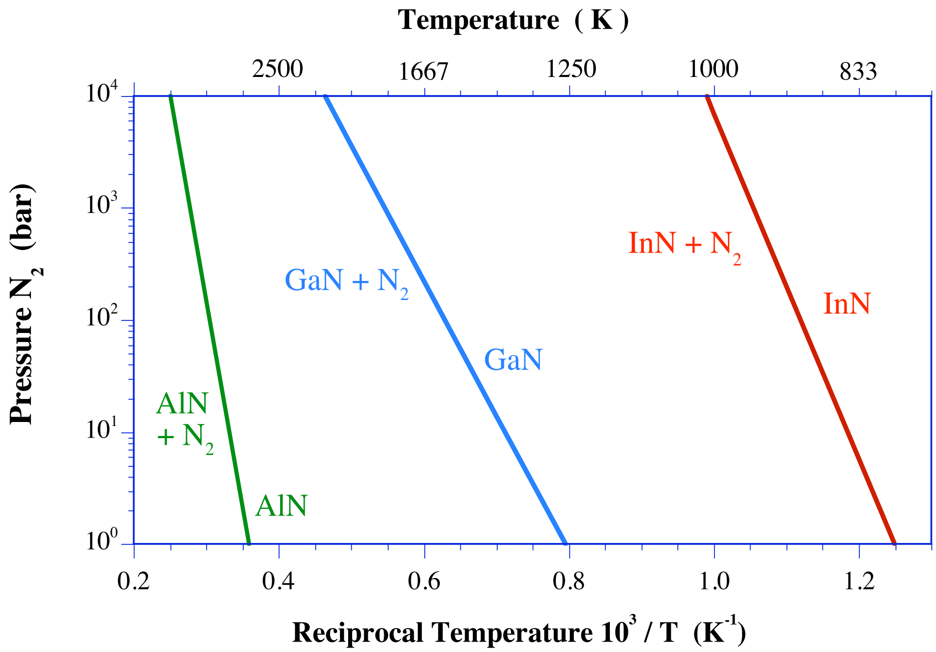

Fig. 1:

Thermal decomposition pressure vs. reciprocal temperature for AlN, GaN and InN[9].

The research program simulated and analyzed various reactor geometries and provided a theoretical assessment of a well-suited high-pressure CVD flow geometry. Based on the predictions, a flow channel reactor design was singled out. The experimental constructed differential HPCVD reactor system is depicted in Fig. 2. In order to confine pressures up to 100 bar, a large outer pressure confinement vessel was required, which made its operation very cumbersome and difficult to control. However, over the three years of operation, significant experience was gained in assessing the flow kinetics of the flow channel and the pressure balancing requirements during inserting of precursor plugs in the gas carrier stream. The knowledge accumulated during this time led to the design of a 2[nd]-generation reactor, the construction of which Drs. Bachmann and Dietz started in 1998. The PI completed the reactor at GSU 2001. The involvement of the PI in the MURI project focused initially on the development of real-time process monitoring[16-18] and control methodology[18,19] using $Ga_{1-x}In_xP$ as an example[20-23]. The involvement expanded as the PI closely interacted with Dr. Bachmann in the design and construction of a compact HPCVD reactor, which is schematically shown in Fig. 3. Besides of the drastic reactor size reduction, the most significant advances implemented in the 2[nd]-generation of HPCVD system were

a) a reduction of the flow channel height from 10 mm to 1 mm,

b) a symmetric flow channel and substrate arrangement, and

c) the integration of optical diagnostics for gas phase and growth surface analysis.

A more detailed description of the reactor design and the optical characterization capabilities can be found at [*"http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html"*](http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html).

The construction of the compact HPCVD reactor was completed at GSU with support of NASA Grant# NAG8-1686 *(from 2000 to 2006; Dr. Bachmann was Co-PI on the project and he retired*

from NCSU in 2003) with a main emphasis on demonstrating the flow kinetics and abilities of the real-time growth diagnostics[24-27].

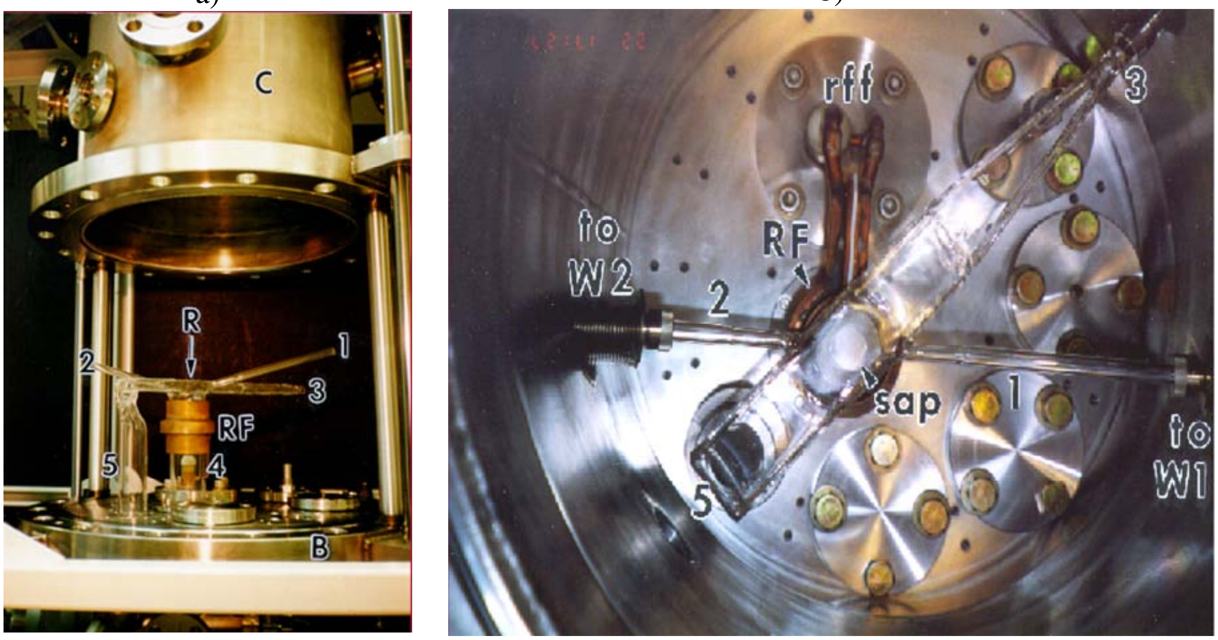

Fig. 2: **a)** 1st generation HPCVD reactor assembly constructed at NCSU in 1996. B = Base Plate; C = 2nd Confinement Shell; R = Fused Silica Reactor; 1&2 = Window Connections for PRS Laser Beams; RF = Radio Frequency Coil; 3&5 = Process Gas Inlet & Outlet; 4 = Tube on R For substrate wafer exchange. **b)** top view of inner flow channel assembly.

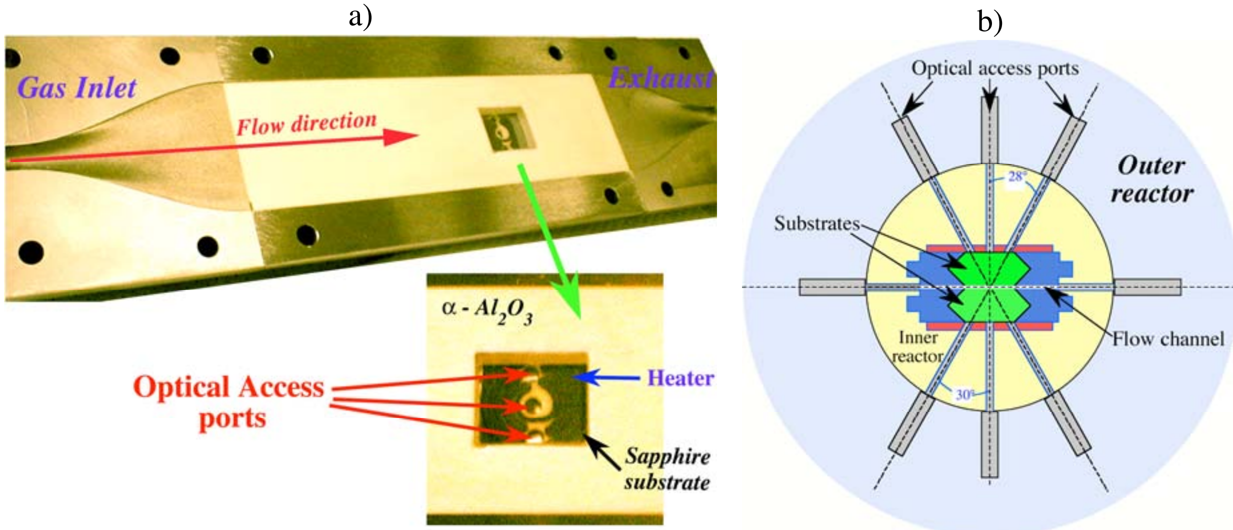

Fig. 3 **a)** 2nd generation HPCVD reactor assembly. The flow channel is designed with a constant cross sectional area for the maintenance of laminar flow and the substrates are embedded in ceramic plates; **b)** Schematic cross section of the reactor containing the optical access ports and the center of the substrates. Optical ports provide access to the flow channel and to the growth surface.

Accessing the growth regime at super-atmospheric pressures brings significant challenges in suppressing gas phase reactions, while controlling the nutrient support through a reduced diffusion layer to the growth surface and optimizing the growth surface chemistry. Chapter 2.3.1 discusses the approaches explored at GSU in more details. An essential component in the exploration of high-pressure CVD growth is the integration of real-time optical characterization techniques that allow to monitor and analyze the gas flow kinetics, the precursor decomposition

dynamics, as well as growth surface reactions. The PI has a long track record of developing optical diagnostic tools[28,29,23] and of applying them for real-time process monitoring[23] and process control[18,19]. For high-pressure CVD, the PI integrated principal angle reflectance spectroscopy (PARS)[30] - a derivation of p-polarized reflectance spectroscopy (PRS)[16], which is able to follow the film growth process with sub-monolayer resolution. The link between the surface sensitive PARS response to the gas phase analysis via ultra-violet absorption spectroscopy (UVAS) allows for the link between gas phase decomposition kinetics and surface chemistry processes, which will provide critical insights in the film growth process at high pressures. With support by AFOSR (award# FA9550-07-1-0345), the PI focused in recent years on the optimization of InN growth in the pressure regime of 10 to 15 bars and in establishing initial results on the processing window of InGaN, the results of which are presented in more details in section 2.3.

InN and InGaN specific material challenges:

InN is predicted to have an electron affinity of 5.8 eV, the largest of any known semiconductor[31]. The consequences of the large electron affinity of InN and indium-rich InGaN can be considered within the amphoteric defect model (ADM). Within the ADM, the formation energy of native defects depends on the location of the Fermi energy (E_F) with respect to a common energy reference, the Fermi stabilization energy (E_{FS}). Therefore, native donor formation is predicted to be dominant in InN and indium-rich InGaN. The low formation energy of native donor defects in InN and indium-rich InGaN creates challenges for producing p-type materials[32]. Degenerate doping may be a solution to achieve p-type InN and indium-rich InGaN, due to the high n-type background of the undoped material.

The pulsed precursor injection scheme employed in HPCVD to minimize gas phase reactions bears also significant advantages for the prevention of phase segregation and for the exploration of the surface chemistry during growth. An important part of this research program will be the investigation of growth kinetics on a micrometer scale, in order to develop a optimum pulse timing. Once this understanding is established, it will be applied to the digital growth of InGaN, which will not only allow the prevention of phase segregation but also the fabrication of III-nitride superlattices[33,34].

For the fabrication of indium-rich $In_{1-x}Ga_xN$ alloys and embedded heterostructures, the thermal stability of InN and indium-rich alloys at growth temperatures that are compatible with GaN growth conditions, needs to be advanced. Our initial InGaN growth results in the pressure regime up to 15 bars (see Chapter 2.3) indicate that pressures above 20 bars may be required - a regime that provides some technical challenges and has not been investigated to date. In this pressure regime, the role of turbulent gas flow becomes decisive.

Another critical issue is the type of growth mode: 2-dimensional (2-dim) versus 3-dimensional (3-dim) film growth. In 2-dim growth mode, material is deposited layer-by-layer. On the other hand, 3-dim growth consists of formation of islands and their subsequent coalescence. The latter results in grain boundaries that detrimentally influence the topographical and electrical properties of the deposited epilayer, e.g., carrier mobility and free carrier concentration[35]. Good topographic properties of $Ga_{1-x}In_xN$ layers (i.e., a smooth surface) are essential for the fabrication of heterostructures. Benchmarks of 3-dim growth are the size, shape, height and density of the islands.

The growth mode during the initial stage of epitaxy (nucleation) is of particular interest, as the quality of the epilayer is governed by the quality of the nucleation layer. Therefore, a good understanding and control of the nucleation and nuclei coalescence is decisive. Moreover, the

growth of $In_{1-x}Ga_xN$ alloys brings along the issue of phase segregation and spinodal decomposition. Our high-pressure CVD approach is promising for enabling new Ga/In ratios (i.e., new x values) that have not been achieved before. Thus phase homogeneity becomes a very important goal of our work. Finally, new alloys may exhibit new defects related to ordering processes in a microscopic scale or cubic/wurtzite lattice instabilities. A careful analysis and identifications of such defects is required. A major effort in our research will pursue a deep understanding of occurring defects, how they differ as a function of growth pressure, and how they affect the materials properties. A beneficial effect of HPCVD is the potential decrease in the native point defect concentrations with increased growth temperature at higher reactor pressures.

The epitaxial growth of ternary III-V systems is characterized by the segregation of one of the constituent column III element at the growth front and at the interfaces with the binary material. This segregation results in poor composition profiles and poor interfacial width control. Chemical stability can be influenced by several factors, a number of which have been explored in the literature, such as heat of formation, ion size, and interfacial strain. The driving force for this segregation in InGaN can be considered to be a replacement reaction of Ga for the In in the substrate. The heat of formation for GaN is –156.8 kcal/mole whereas that for InN is –28.6 kcal/mole. The ejection of In from an underlying InGaN layer with Ga deposition thus results in a lower free energy for the surface. The transport of In to the surface is mediated by the surface exchange of Ga for In. The lower free energy of the GaN layer accounts for the asymmetry in the In diffusion profile with growth order in compositional modulated structures. This preferential segregation may be limited by migration enhanced epitaxy techniques in MBE and by variation of the III/V ratio in MOCVD and CBE. Segregation is also seen with annealing processes and current injection techniques.

Other aspects of scientific interest arise from the strong polarity of Group III-nitride crystals. A higher concentration of indium in InGaN/GaN quantum wells (QW) results in more strain and more polarization[36]. The quantum confined Stark effect (QCSE) is caused by spontaneous polarization and by a strain induced piezoelectric field. Increasing the indium composition increases the piezoelectric field[37]. The resulting QCSE will cause a blue shift at high current densities moving further away from the desired wavelength, and at lower current densities, efficiency will be low due to charge separation[37-39].

The challenges given by the stabilization of indium-rich group III-nitride alloys and embedded heterostructures in wide bandgap group III-nitrides (e.g., $In_{1-x}Ga_xN$) can be addressed by the PI's successful development of an advanced 2nd-generation version of the high-pressure growth reactor capable of operating at pressures of up to 100 bar. The pulsed injection of precursor gases is a prerequisite for high-pressure operation and, at the same time, it facilitates control of the growth process on sub-monolayers, as well the thorough investigation of surface processes during growth.

II. Accomplishments

Growth of InN and InGaN under high-pressure CVD conditions - present status

InN layer characterization

A promising approach to tackle the challenges outlined in the previous section has been developed by the PI at Georgia State University. A unique high-pressure chemical vapor deposition (HPCVD) reactor allows the extension of the thin film growth parameter space by utilizing the pressure dependency[27,40,41] (up to 100 bar) of chemical reactions. Growing indium-rich $In_{1-x}Ga_xN$ alloys at high pressures and high temperatures (T > 850 °C) is promising since this approach may overcome problems of off-equilibrium techniques arising from different partial pressures and low growth temperatures. Over the last years the PI's research group demonstrated the capability of HPCVD to produce high-quality, single-phase InN layers. As depicted in Fig. 3, InN layers exhibit XRD (0002) Bragg reflexes with a full width at half maximum (FWHM) below 200 arcsec and rocking curve values around 1600 arcsec. Further rocking curve analysis for the symmetric and skew-symmetric reflections indicate that - within the experimental resolution - InN grew single phase and epitaxially on the GaN template. A reciprocal XRD map scan - depicted in Fig. 5 - shows a nearly relaxed InN epilayer on top of GaN.

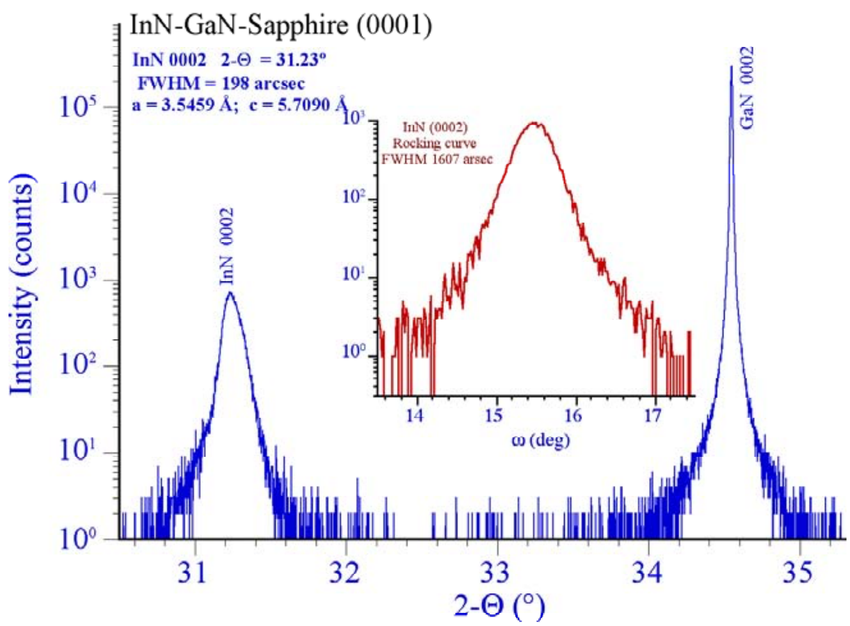

Fig. 4:

FWHM's of 2Θ-ω XRD Bragg reflex and rocking curve on an InN layer grown by HPCVD at 850°C and 15 bar reactor pressure.

The free electron concentrations in the InN layers are assessed via IR reflectance spectroscopy, which allows to extract the dielectric functions of the layers in the IR regime and to analyze the phonon contribution, as well as the plasma permittivity,[42,43] The fit of the IR spectra provides supplemental (to Raman spectroscopy) structural data on the LO and TO frequencies of the E_1 phonon mode, as well as data on the average free electron concentrations and mobility in the layers. The best-fit approximation of the InN epilayer reveals a InN free electron concentration in the low 10^{19} cm^{-3} range *(not corrected for any interfacial electron accumulation effects)*, with a carrier mobility μ_c of 434 $cm^{-2}V^{-1}s^{-1}$. The relatively high free carrier concentration was thought to be related to residual oxygen incorporation, an issue addressed by adding additional purification filters. However, recent studies by low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS)[44-46 47] suggest that in incorporation of hydrogen (via

the ammonia precursor) in the InN layer may significantly contribute to the high free carrier concentrations in OMCVD[48] and HPCVD grown layers.

InN samples grown on sapphire - but otherwise similar conditions - show typically smaller free electron concentration in the low to mid 10^{18} cm^{-3}, a phenomenon presently not well understood and will be explored further. As shown in Fig. 6, a photoluminescence (PL) spectrum is observed at 0.77 eV with a FWHM of 0.02 eV. Since the germanium detector used has a sharp fall-off at 0.75 eV, further features at lower energies cannot be ruled out. The luminescence is in good agreement with absorption measurements, which shows an absorption edge below 0.8 eV.

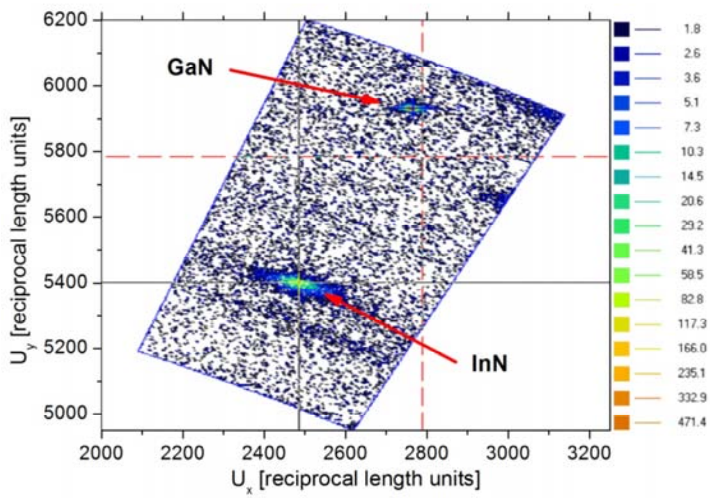

Figure 5: Reciprocal map scan shows nearly relaxed InN on top of GaN. Analysis for the symmetric and skew-symmetric reflections indicate that the InN epilayer grew single phase and epitaxially on the GaN template.

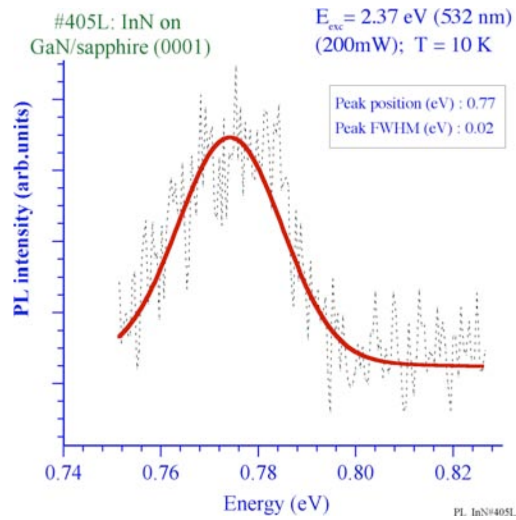

Figure 6: PL spectra of an InN layer grown on a GaN on sapphire template (fall-off below 0.75 eV due to Ge detector limitations)

So far, the growth of InN has been explored in the laminar flow regime, evaluating the growth parameter for reactor pressures in the range of 10 to 15 bars, gas flow velocities from 20-50 cms^{-1}, and molar ammonia to trimethylindium (TMI) ratios between 200 to 8000. Even though the structural quality is already very good, the high free carrier concentrations found in these layers need to be reduced significantly, a task that will require a detailed understanding on how the growth surface chemistry relates to the point defect chemistry in the grown material (a research program proposed to NSF DMS). For this, real-time optical characterization techniques are employed that are able to follow the film growth process with sub-monolayer resolution. As discussed above and in section 2.3.2, the link between the surface sensitive PARS response to the real-time gas phase analysis (UVAS) will provide crucial insights in the gas phase decomposition kinetics, surface chemistry processes, and physical properties of the grown bulk layers.

InGaN layer characterization

High quality InN layers were achieved for growth temperatures in the range of 830°C to 850°C, which is about 250°C higher than under low-pressure OMCVD conditions. To assess the thermal stability of indium-rich $In_{1-x}Ga_xN$ alloys at the InN growth temperature of 850°C, a series of $In_{1-x}Ga_xN$ alloys were grown at 850°C and 15 bar reactor pressure. The XRD analysis for selected indium-rich $In_{1-x}Ga_xN$ layers from $0 < x < 0.65$ are summarized in Fig. 7.

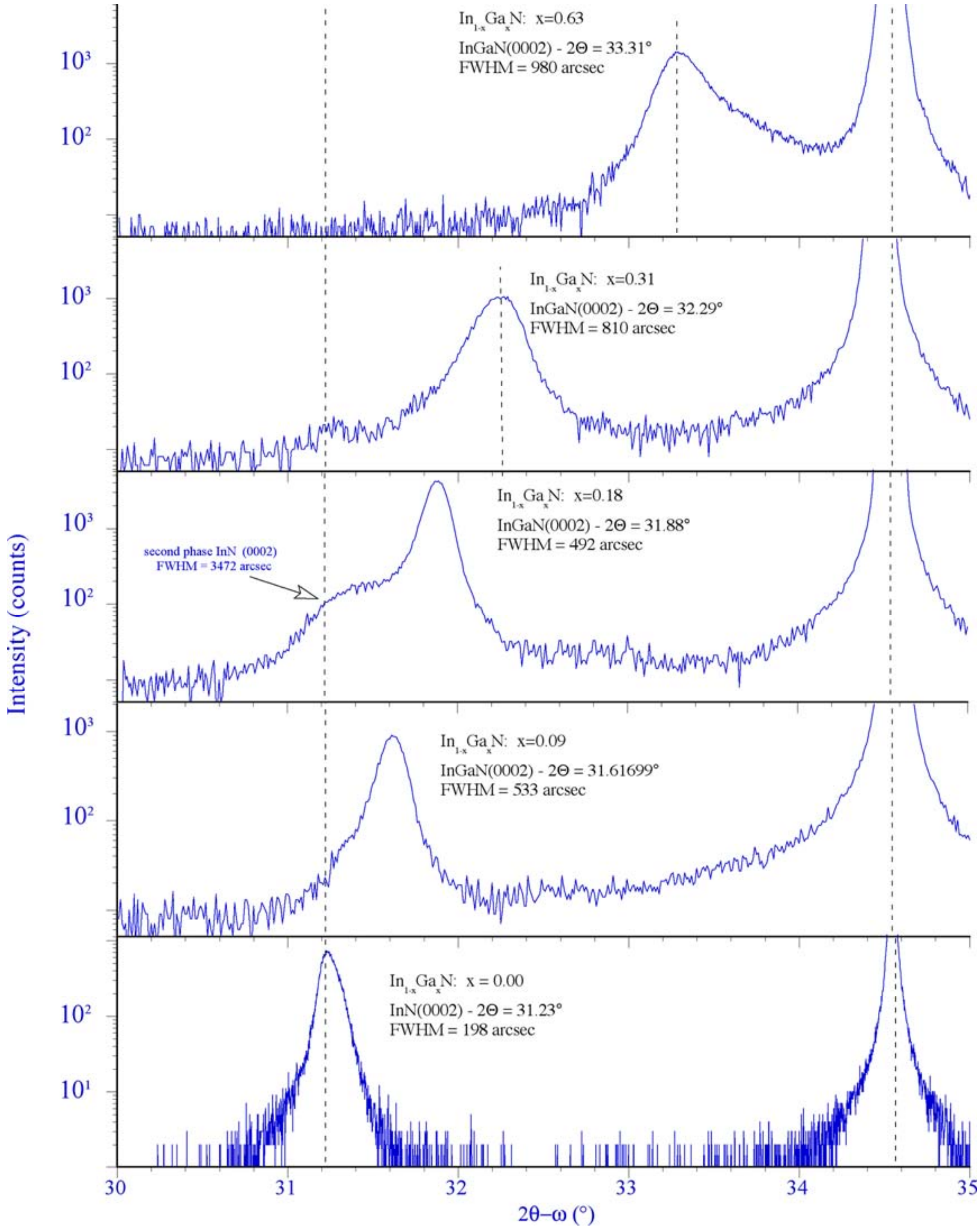

Figure 7: $In_{1-x}Ga_xN(0002)$ Bragg reflexes of XRD 2Θ-ω scans for $In_{1-x}Ga_xN$ layer grown by high-pressure CVD at 850°C and 15 bar reactor pressure.

Under these pressure and temperature conditions, macroscopic InN-InGaN phase segregations have been observed in the compositional regime $0.1 < x < 0.30$, while macroscopic a single-phase material can be obtained in the compositional regime $0.3 < x < 0.65$. The ω -scan InGaN(0002) rocking curve analysis reveals FWHM's around 5000 – 7000 arcsec (x=0.31), indicating a high density of point defects and dislocations. Interestingly, the $In_{1-x}Ga_xN$ phase segregations observed differ for $In_{1-x}Ga_xN$ growth on GaN versus sapphire, indicating that not only the pressure/temperature processing parameter contributes to the segregation process. Potentially, induced lattice strain, interfacial piezoelectric polarization effects, and extended defects may contribute to the compositional fluctuations.

To improve the thermal stability of indium-rich alloys at the desired growth temperatures that are compatible with GaN growth conditions, the growth may have to be expanded to reactor pressures well above 20 bar. Even though this pressure regime inevitably leads to turbulent growth flow conditions, the potential benefits will be the merged temperature processing window that allows the fabrication of indium rich $In_{1-x}Ga_xN$ alloys with wider bandgap group III-nitride layers, an essential step for many of the envisioned device structures.

Indium add-layer problem

The indium adlayer formation[49-51] during InN and InGaN growth is a well-known phenomenon. Its ability to act as surfactant has been described for the AlGN/GaN heterostructure growth.[52]
Figure 8 shows the 2Θ-ω XRD scans for a InN layer grown on a GaN template before and after etching in a HCl:H_2O (1:10) solution. The In(101) Bragg reflex disappears after typically 2 min etch time, indicated the complete removal of the surface indium.
For the growth of InGaN and InGaN/GaN heterostructures, however, it has to be avoided, requiring precise adjustments of the surface chemistry (precursor pulse separation, growth temperature, reactor pressure). Initial studies during InN growth showed that the indium adlayer formation can be suppressed by adjusting the precursor injection sequence. Detailed studies are required to optimize the surface chemistry for each InGaN target composition.

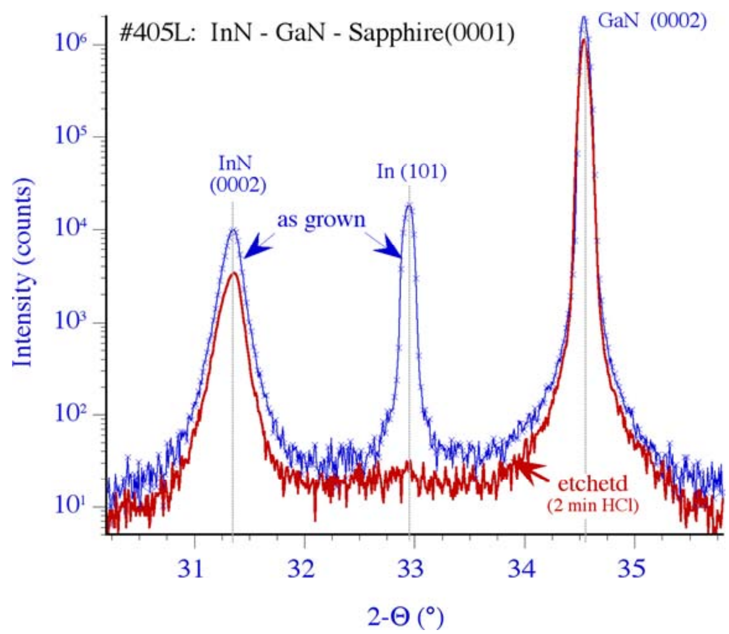

Figure 8:

XRD Bragg reflex of InN(101) is related to an indium adlayer formed during InN growth on a GaN template. The indium add-layer is completely removed by a 2 min HCl:H_2O (1:10) etch.

2.3.2 Real-time growth control and optical growth monitoring

The progress in understanding and controlling thin film growth processes has been very slow, considering how little is known about chemical reaction pathways and reaction kinetic~~s~~ parameters during the decomposition process of the metal-organic (MO) precursors.
These demands led to the development of advanced surface-sensitive optical diagnostics that can be integrated in CVD reactors[53,54,23,26]. These diagnostic techniques move the monitoring and control point close to where the growth occurs which, in a chemical beam epitaxy process, is the surface reaction layer, built up of physisorbed and chemisorbed precursor fragments between the ambient and film interface. In recent years, we developed and explored p-polarized reflectance spectroscopy (PRS)[23,16,55] as a highly surface sensitive sensing technique, and demonstrated the closed-loop control of deposition processes at low pressure pulsed chemical beam epitaxy[22].

With advancing progress in the growth of indium-rich $In_{1-x}Ga_xN$, the employed optical real-time monitoring techniques will allow for the investigation of fundamental questions regarding surface chemistry. In this context, the competing incorporation of In and Ga atoms is of particular interest for an understanding of compositional questions and segregation processes. During the growth of $In_{1-x}Ga_xN$/GaN heterostructures, we will be able to investigate the physical and chemical processes during the transition from indium-rich to gallium-rich $In_{1-x}Ga_xN$ layers which govern the quality of such heterostructures and which will bring upon clarity about the interfacial phenomena discussed above.

The approach taken at GSU is to develop and utilize real-time optical diagnostic techniques - as well as a pulsed precursor injection scheme - to gain insights and to control the gas phase and surface chemistry processes that govern the growth of InN and indium-rich group III-nitride alloys. This will be of crucial importance for understanding and controlling their materials properties. For the described high-pressure CVD growth reactor, we developed "principal angle reflectance spectroscopy" (PARS),[30] and we utilize ultra-violet absorption (UVA) spectroscopy to analyze the kinetics of gas phase constituents above the growth surface.[26] Fig. 9a shows a typical precursor pulsing sequence employed during the growth of InN and InGaN, where the metal precursors are injected simultaneously. The UVA trace shown in Fig. 9b is monitored in real-time, at a wavelength where the precursor shows characteristic absorption. As depicted in Fig. 9b, the precursor arrival above the growth surface can be observed in the UVA trace and correlated to each precursor constituent. The control of the injection sequence shown in Fig. 9a - together with the real-time UVA trace analysis - enables the precise engineering of gas phase and surface reactions, an essential tool to optimize the process conditions.

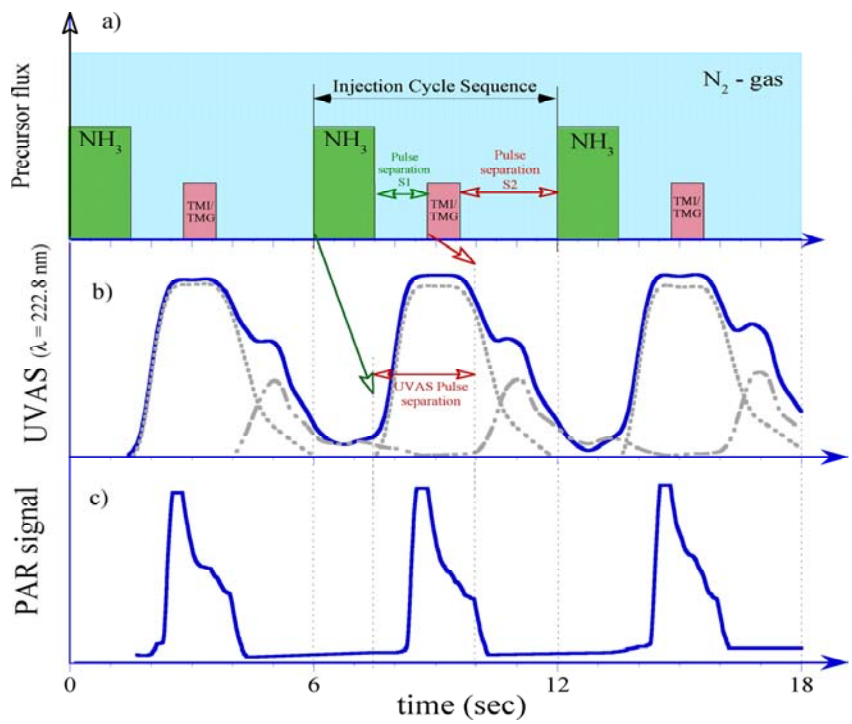

Figure 9:

a) A representative precursor flux injection scheme used during InN and InGaN growth and

b) the real-time ultra-violet absorption trace monitored above the growth surface at 222.8 nm during steady-state InGaN growth conditions. The TMI and trimethylgallium (TMG) precursors are injected simultaneously

c) growth surface response via PARS signal

The link between the surface sensitive PARS response to the real-time gas phase analysis (UVAS) will provide crucial insights in the gas phase decomposition kinetics, surface chemistry processes, and the film growth process at high pressures. Advanced growth models as established for the growth of GaInP[23] are envisioned and will be essential for the exploration of high-pressure growth process parameters. As shown, adjusting the pulse separations between the

precursors - as well as the length of each precursor pulse - are additional process control parameters that may be utilized in optimizing surface chemistry and materials properties.[56]

InGaN gas phase and surface chemistry at elevated reactor pressures

The formation of $In_{1-x}Ga_xN$ ternary alloys in the whole composition range is of great interest, since it would allow to tune the direct bandgap from the near infrared (InN around 0.7 eV) to the near UV wavelength regions (GaN at 3.5 eV). However, experimental and theoretical predictions indicate that the $In_{1-x}Ga_xN$ ternary alloys might be unstable with a tendency toward clustering and phase separations.[57] For instance, it is well known that indium phase separation (or fluctuation) induced localized states in the InGaN layers play major roles in achieving highly efficient blue and green InGaN multiple quantum wells (MQW).

The large differences in the tetrahedral radii between InN and GaN may induce strain that can either lead to the formation of particular sublattices (phase separations) or to an atomic ordering within the sublattice, resulting in a deviation from homogeneity (nano-clustering).[58,57]

Nevertheless, the growth of single phase $In_{1-x}Ga_xN$ alloys by rf-PMBE at growth temperatures between 400-435°C has been demonstrated by Iliopoulos et al.[59] in the entire composition range, which suggests that under proper processing conditions, clustering and phase separations in the ternary InGaN alloy system can be suppressed. Under low-pressure MOCVD growth conditions with typical growth temperatures between 700 and 800 °C, metastable $In_{1-x}Ga_xN$ alloys are predicted for regions of low and high gallium concentrations ($0.94>x<0.64$ and $0.1>x<0.3$) and compositional unstable $In_{1-x}Ga_xN$ alloy regions, where phase separations occur due to spinoidal decomposition.[57] Contrary to these predictions, recent $In_{1-x}Ga_xN$ layers grown by MOCVD indicate that single phase $In_{1-x}Ga_xN$ alloys in the compositional range $0.33 > x < 0.75$ can be achieved by adjusting the growth temperature as function of composition (i.e., x).[60,61]

The question left open is whether a processing window exists where $In_{1-x}Ga_xN$ layers with different compositions can be stabilized at the same growth temperature. The high-pressure CVD reactor system explored here - together with the digital injection system - may provide the pathway to establish such common processing window,

a) by adjusting the reactor pressure to stabilize a compositional alloy at the temperatures at which the alloy would either decompose or exhibit phase separation

b) by adjusting the group V/III precursor ratio and surface chemistry as function of composition x with sub-monolayer precision as outlined in Fig. 9 and Fig. 10.

An additional process control parameter in the growth of ternary or quaternary alloys such as InGaN or InGaAlN is illustrated in Fig. 10. Here, the injection of the metal precursors, TMI and TMG, are separated in different sequences.

The major advantages are that:

- each sequence is uniquely tailored to the gas and surface chemistry of the alloy formed, e.g., each sequence can have a unique timing for pulse separations;
- by adjusting the precursor pulse lengths, each sequence can have a unique group V/III precursor ratio that is tailored to the specific partial pressures;
- each of the sequences can be repeated numerous times, in order to deposit the specific amount of material to be engineered:
    - the targeted material composition,
    - the materials alloying / intermixing process,
    - the phase segregation process in dissimilar materials, or
    - the formation of straight or compositional graded quantum wells.

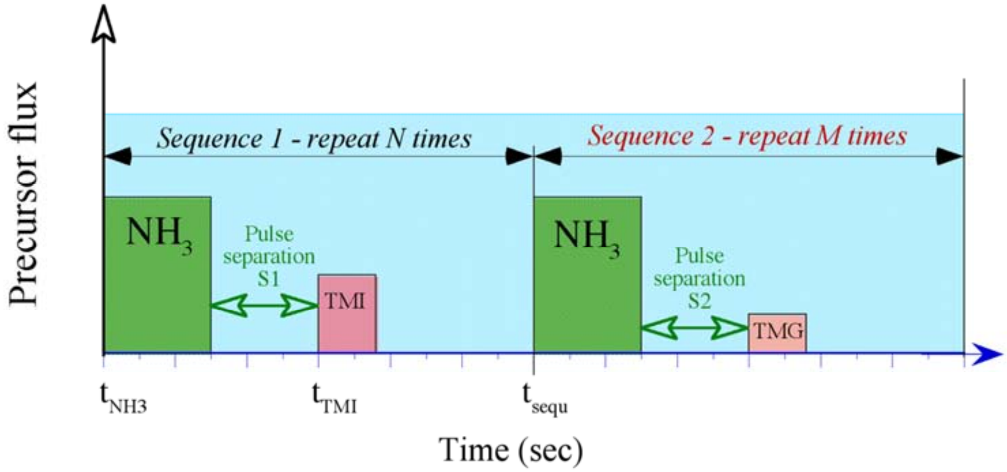

Figure 10: Precursor flux injection arrangement using separate group III-precursor injections. Such growth schemes will be explored for the evaluation of digital InGaN alloy formation, for the control of phase segregations, as well as to adjust the injection parameter to the different TMI and TMG growth chemistry on a sub-monolayer level.

Citations:

[1] T. P. Bartel and C. Kisielowski, "A quantitative procedure to probe for compositional inhomogeneities in $In_xGa_{1-x}N$ alloys," Ultramicroscopy 108, 1420 (2008).

[2] M. G. Ganchenkova, V. A. Borodin, K. Laaksonen, and R. M. Nieminen, "Modeling the compositional instability in wurtzite Ga[sub 1 - x]In[sub x]N," Phys. Rev. B 77, 075207 (2008).

[3] J. Zheng and J. Kang, "Theoretical study of phase separation in wurtzite InGaN," Materials Science in Semiconductor Processing 9, 341 (2006).

[4] M.-K. Chen, Y.-C. Cheng, J.-Y. Chen, C.-M. Wu, C. C. Yang, K.-J. Ma, J.-R. Yang and A. Rosenauer, "Effects of silicon doping on the nanostructures of InGaN/GaN quantum wells," J. Cryst. Growth 279(1-2) pp.55-64 (2005).

[5] S. Yu. Karpov, "Suppression of phase separation in InGaN due to elastic strain," MRS Internet J. Nitride Semicond. Res. 3, 16(1998).

[6] N. A. El-Masry, E. L. Piner, S. X. Liu, and S. M. Bedair, "Phase separation in InGaN grown by metalorganic chemical vapor deposition," Applied Physics Letters 72, 40 (1998).

[7] I. Ho and G.B. Stringfellow, "Solid phase immiscibility in GaInN," Appl. Phys. Lett. 69 p. 2701-03 (1996).

[8] G. Stringfellow, "Spinodal decomposition and clustering in III/V alloys," Journal of Electronic Materials 11(5), pp.903-918 (1982).

[9] J. MacChesney, P.M. Bridenbaugh, and P.B. O'Connor, "Thermal stability on Indium Nitride at elevated temperatures and nitrogen pressures," Mater. Res. Bull. 5 pp. 783-792 (1970).

[10] B. Onderka, J. Unland, R. Schmid-Fetzer, "Thermodynamics and Phase Stability in the In-N System," J. Mater. Res. 17, 3065-3083 (2002).

[11] K.J. Bachmann, S. McCall, S. LeSure, N. Sukidi and F. Wang, J. Jpn. Soc. Microgravity Appl. Vol. 15 p. 436 (1998).

[12] K.J. Bachmann and G. Martinelli-Kepler, "Heteroepitaxy at High and Low Pressure", Proc. SPIE, Vol. 3123 (1997) 64-74.

[13] G. M. Kepler, C. Höpfner, J. S. Scroggs and K. J. Bachmann, "Simulation of a vertical reactor for high pressure organometallic chemical vapor deposition," Mater. Sci. & Eng. B 57(1) pp. 9-17 (1998).

[14] K. J. Bachmann, H. T. Banks, C. Hopfner, G. M. Kepler, S. LeSure, S. D. McCall and J. S. Scroggs, "Optimal design of a high pressure organometallic chemical vapor deposition reactor," Mathematical and Computer Modelling 29(8) pp. 65-80. (1999).

[15] K. J. Bachmann, B. H. Cardelino, C. E. Moore, C. A. Cardelino, N. Sukidi, S. McCall "Modelling and Real-Time Process Monitoring of Organometallic Chemical Vapor Deposition of III-V Phosphides and Nitrides at Low and High Pressures," Mat. Res. Soc. Symp. Proc. Vol. 569 pp.59-70 (1999).

[16] N. Dietz and K. J. Bachmann, "p-Polarized reflectance spectroscopy: a highly sensitive real-time monitoring technique to study surface kinetics under steady state epitaxial deposition conditions", Vacuum 47, pp. 133-140 (1996).

[17] N. Dietz, N. Sukidi C. Harris and K.J. Bachmann, "Real-time Monitoring of Surface Processes by P-Polarized Reflectance", J. Vac. Sci. Technol. A 15 p. 807 (1997).

[18] N. Dietz, K. Ito, Real-time optical characterization of GaP heterostructures by p-polarized reflectance, Thin Solid Films 313-314, p. 615-620 (1998).

[19] S. Beeler, H.T. Tran and N. Dietz, "Representation of GaP Formation by a Reduced Order Model using P-Polarized Reflectance Measurements", J. Appl. Phys. 86(1), pp. 674-682 (1999).

[20] N. Dietz, V. Woods, K. Ito and I. Lauko, "Real-Time Optical Control of $Ga_{1-x}In_xP$ Film Growth by P-Polarized Reflectance," J. Vac. Sci. Technol. A 17(4), pp. 1300-1306 (1999).

[21] V. Woods, K. Ito, I. Lauko and N. Dietz, "Real-time thickness and compositional control of $Ga_{1-x}In_xP$ growth using p-polarized reflectance", J.Vac. Scien. & Techn. A, 18(4) pp. 1190-1195 (2000).

[22] N. Dietz, S.C. Beeler, J.W. Schmidt and H.T. Tran, "Surface reaction kinetics of Ga1-xInxP growth during pulsed chemical beam epitaxy," Appl. Surf. Sci. 178(1-4), pp 63-74 (2001).

[23] N. Dietz, "Real-time optical Characterization of thin film growth," Mater. Sci. & Eng. B87(1), pp.1 - 22 (2001).

[24] N. Dietz, V. Woods, S. McCall and K.J. Bachmann, "Real-time optical monitoring and simulation of gas phase kinetics in InN vapor phase epitaxy at high pressure," Proc. Microgravity Conf. 2002, NASA/CP-2003-212339, pp. 169 -181 (2003).

[25] N. Dietz, M. Strassburg and V. Woods, "Real-time Optical Monitoring of Ammonia Decomposition Kinetics in InN Vapor Phase Epitaxy at Elevated Pressures," J. Vac. Sci. Technol. A 23(4) pp. 1221-1227 (2005).

[26] V. Woods and N. Dietz, "InN growth by high-pressures chemical vapor deposition: Real-time optical growth characterization," Mater. Sci. & Eng. B 127(2-3) pp 239-250 (2006).

[27] "Indium-nitride growth by HPCVD: Real-time and ex-situ characterization," N. Dietz, book chapter 6 in "III-Nitrides Semiconductor Materials", ed. Z.C. Feng, Imperial College Press, ISBN 1-86094-636-4, pp. 203-235 (2006).

[28] N. Dietz and H.J. Lewerenz, "An optical in-situ method for layer growth characterization", Appl. Surf. Sci. 69, 350-354 (1993).

[29] K.J. Bachmann, N. Dietz and A.E. Miller, "Methods for Monitoring and Controlling Deposition and Etching using P-Polarized Reflectance Spectroscopy", US Patent Number 5,552,327 (1996).

[30] N. Dietz, S. McCall, K.J. Bachmann, “Real-time optical monitoring of flow kinetics and gas phase reactions under high-pressure OMCVD conditions," Proc. Microgravity Conf. 2000, NASA/CP-2001-210827, pp. 176 -181 (2001).

[31] J. W. A. Iii, R. E. Jones, D. M. Yamaguchi, K. M. Yu, W. Walukiewicz, S. X. Li, E. E. Haller, H. Lu, and W. J. Schaff, "p-type InN and In-rich InGaN," Phys. Stat. Sol. (b) 244(6) pp.1820-1824 (2007).

[32] M. Gunes, N. Balkan, D. Zanato, W.J. Schaff, "A comparative study of electrical and optical properties of InN and In0.48Ga0.52N," Microelectronics Journal 40(4-5) pp.872-874 (2009).

[33] D.J. As, Cubic group-III nitride-based nanostructures--basics and applications in optoelectronics, Microelectronics Journal, Volume 40, Issue 2, Wide Band Gap Semiconductor Nanostructures for Optoelectronic Applications, February 2009, Pages 204-209

[34] S. Choi, H. J. Kim, J.-H. Ryou, and R. D. Dupuis, "Digitally alloyed modulated precursor flow epitaxial growth of AlxGa1-xN layers with AlN and AlyGa1-yN monolayers," J. Cryst. Growth 311(12) pp. 3252-3256 (2009).

[35] V. Lebedev et al., "Effect of island coalescence on structural and electrical properties of InN thin films," J. Cryst. Growth 300, pp. 50-56 (2007).

[36] Akihiko Yoshikawa, Songbek Che, Yoshihiro Ishitani, Xinqiang Wang, "Advances in InN epitaxy and its material control by MBE towards novel InN-based QWs," Journal of Crystal Growth 311(7) pp.2073-2079 (2009).

[37] T. Takeuchi, S. Sota, M. Katsuragawa, M. Komori, H. Takeuchi, H. Amano and I. Akasaki, "Quantum-Confined Stark Effect due to Piezoelectric Fields in GaInN Strained Quantum Wells," Jpn. J. Appl. Phys. 36, L382-L385 (1997).

[38] S. Chichibu, T. Azuhata, T. Sota, S. Nakamura, "Spontaneous emission of localized excitons in InGaN single and multiquantum well structures," Appl. Phys. Lett. 69(27) pp.4188-4190 (1996).

[39] S. Chichibu et al, "Origin of defect-insensitive emission probability in In-containing (Al,In,Ga)N alloy semiconductors," Nature Materials 5, pp. 810-816 (2006)

[40] M. Alevli, G. Durkaya, W. Fenwick, A. Weerasekara, V. Woods, I. Ferguson, A.G.U. Perera and N. Dietz, “The characterization of InN layers grown by high-pressure chemical vapor deposition,” Appl. Phys. Lett. 89, pp. 112119 (2006).

[41] N. Dietz, M. Alevli, R. Atalay, G. Durkaya, R. Collazo, J. Tweedie, S. Mita, and Z. Sitar, "The influence of substrate polarity on the structural quality of InN layers grown by high-pressure chemical vapor deposition,", Appl. Phys. Lett. 92(4) pp. 041911-3 (2008).

[42] J. S. Thakur, G. W. Auner, D. B. Haddad, R. Naik, and V. M. Naik, "Disorder effects on infrared reflection spectra of InN films," J. Appl. Phys. 95(9) pp. 4795-4801 (2004).

[43] Z. G. Hu, M. Strassburg, A. Weerasekara, N. Dietz, A. G. U. Perera, M. H. Kane, A. Asghar, and I. T. Ferguson, “Lattice vibrations in hexagonal Ga1-xMnxN epitaxial films on c-plane sapphire substrates by infrared reflectance spectra,” Appl. Phys. Lett. 88, pp.061914-6 (2006).

[44] R.P. Bhatta, B.D. Thoms, M. Alevli and N. Dietz, "Desorption of hydrogen from InN observed by HREELS," Surface Science 602(7) , pp.1428-1432 (2008).

[45] R.P. Bhatta, B.D. Thoms, M. Alevli and N. Dietz, "Surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition," Surf. Sci. 601, pp. L120–L123 (2007).

[46] R. P. Bhatta, B. D. Thoms, A. Weerasekera, A. G. U. Perera, M. Alevli, and N. Dietz, “Carrier concentration and surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition,” JVST A 25(4) pp. 967-970 (2007).

[47] R. P. Bhatta, B. D. Thoms, M. Alevli, V. Woods, and N. Dietz, "Surface structure, composition, and polarity of indium nitride grown by high-pressure chemical vapor deposition," Appl. Phys. Lett. 88 pp.122112-3 (2006).

[48] S. Ruffenach, M. Moret, O. Briot, and B. Gil, "Ammonia: A source of hydrogen dopant for InN layers grown by metal organic vapor phase epitaxy," Appl. Phys. Lett. 95(4) pp.042102-3 (2009).

[49] Huajie Chen, R. M. Feenstra, J. E. Northrup, J. Neugebauer, and D. W. Greve, "Indium incorporation and surface segregation during InGaN growth by molecular beam epitaxy," Mat. Res. Soc. Symp. Vol. 639 pp.G2.6.1-6 (2001).

[50] D. Segev and C. G. Van de Walle, "Surface reconstructions on InN and GaN polar and nonpolar surfaces," Surface Science 601(4) pp.L15-L18 (2007).

[51] S. Choi, T.-H. Kim, S. Wolter, A. Brown, H. O. Everitt, M. Losurdo, and G. Bruno, "Indium adlayer kinetics on the gallium nitride (0001) surface: Monitoring indium segregation and precursor-mediated adsorption," Phys. Rev. B 77(11) pp.115435-7 (2008).

[52] E. Monroy, N. Gogneau, E. Bellet-Amalric, F. Enjalbert, J. Barjon, D. Jalabert, J. Brault, Le Si Dang, and B. Daudin, "In as a Surfactant for the Growh of AlGaN/GaN Heterostructures by Plasma Assisted MBE," Mat. Res. Soc. Symp. Proc.743 p. L6.1.1-6 (2003).

[53] I. P. Herman, "Optical Diagnositcs for thin Film Processing " (Academic Press Inc., New York, 1996).

[54] D. E. Aspnes and N. Dietz, "Optical Approaches for Controlling Epitaxial Growth", Applied Surface Science 130-132 pp. 367-376 (1998).

[55] N. Dietz and K. J. Bachmann, "Real -time monitoring of epitaxial processes by parallel-polarized reflectance spectroscopy", MRS Bull. 20, p.49 (1995).

[56] M. Buegler, M. Alevli, R. Atalay, G. Durkaya, I. Senevirathna, M. Jamil, I. Ferguson, and N. Dietz, "Optical and structural properties of InN grown by HPCVD," Proc. SPIE Vol. 7422 p. 742218 (2009).

[57] Ayan Kar, Dimitri Alexson, Mitra Dutta, and Michael. A. Stroscio, "Evidence of compositional inhomogeneity in $In_xGa_{1-x}N$ alloys using ultraviolet and visible Raman spectroscopy.," J. Appl. Phys. 104, 073502 (2008).

[58] I. H. Ho, G. B. Stringfellow, "Incomplete solubility in nitride alloys", Materials Research Society Symposium Proceedings 449, p. 871 (1997).

[59] E. Iliopoulos, A. Georgakilas, E. Dimakis, A. Adikimenakis, K. Tsagaraki, M. Androulidaki, and N. T. Pelekanos, "InGaN(0001) alloys grown in the entire composition range by plasma assisted molecular beam epitaxy," physica status solidi (a) 203(1) pp.102-5 (2006).

[60] B. N. Pantha, J. Li, J. Y. Lin, and H. X. Jiang, "Single phase In[sub x]Ga[sub 1 - x]N (0.25 <= x <= 0.63) alloys synthesized by metal organic chemical vapor deposition," Appl. Phys. Lett. 93(18), p.182107 (2008).

[61] R. Dahal, B. Pantha, J. Li, J. Y. Lin, and H. X. Jiang, "InGaN/GaN multiple quantum well solar cells with long operating wavelengths," Appl. Phys. Let. 94(6) pp. 063505-3 (2009).

III. Publications of research results

III.1 Patent filed

A provisional patent application, entitled "Improved method and apparatus for performing high pressure chemical vapor deposition" has been filed Aug. 12, 2009.

III.2 Completed theses

Dr. Goksel Durkaya (PhD in Physics at GSU - completed Dec. 04, 2009)
PhD Title: "Nanoscopic investigation of surface morphology of neural growth cones and InGaN semiconductor alloys."

Dr. Mustafa Alevli (PhD in Physics at GSU - completed Feb. 04, 2008)
PhD Title: "Growth and characterization of indium nitride layers grown by high-pressure chemical vapor deposition,"

III.3 Referred Publications (published) during award period:

9 "Growth temperature - phase stability relation in $In_{1-x}Ga_xN$ epilayers grown by high-pressure CVD," G. Durkaya, M. Alevli, M. Buegler, R. Atalay, S. Gamage, M. Kaiser, R. Kirste, A. Hoffmann, M. Jamil, I. Ferguson and N. Dietz, Mater. Res. Soc. Symp. Proc. 1202, pp.1-6 (2010).

8 "Optical and structural properties of InN grown by HPCVD," M. Buegler, M. Alevli, R. Atalay, G. Durkaya, I. Senevirathna, M. Jamil, I. Ferguson, and N. Dietz, Proc. SPIE 7422, 742218 (2009).

7 "Optical Characterization of InN Layers Grown by High-Pressure Chemical Vapor Deposition," M. Alevli, G. Durkaya, R. Atalay, R. Kirste, A. Weerasekara, A. G. U. Perera, A. Hoffmann and N. Dietz, J. Vac. Sci. Technol. A 26(4), pp. 1023-1026 (2008).

6 "Desorption of hydrogen from hydrogenated indium nitride surface observed by HREELS," R. P. Bhatta, B. D. Thoms, M. Alevli, and N. Dietz, Surf. Sci. **602**(7), pp.1428-1432 (2008).

5 "The influence of substrate polarity on the structural quality of InN layers grown by high-pressure CVD," N. Dietz M. Alevli, R. Atalay, and G. Durkaya, R. Collazo, J. Tweedie, S. Mita, and Z. Sitar, Appl. Phys. Lett. 92(4) pp. 041911-3 (2008).

4 "Structure of Isolated Oxygen Impurity States in InN," D. Alexandrov, S. Butcher N. Dietz and H. Yu, Mat. Res. Soc. Symp. Proc. 1040E, Symposium Q: Nitrides and Related Bulk Materials, Boston, MA, USA, Nov. 26-30. 2007, Paper# 1040E-Q9.15, pp. 1-6 (2008).

3 "Surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition," R. P. Bhatta, B. D. Thoms, M. Alevli, and N. Dietz, Surf. Sci. 601, pp. L120–L123 (2007).

2 "Carrier concentration and surface electron accumulation in indium nitride layers grown by high pressure chemical vapor deposition," R. P. Bhatta, B. D. Thoms, A. Weerasekera, A. G. U. Perera, M. Alevli, and N. Dietz, J. Vac. Sci. Technol. A **25**(4) pp. 967–970 (2007).

1 "Properties of InN layers grown by High Pressure CVD," M. Alevli, G. Durkaya, R. Kirste, A. Weesekara, W. E. Fenwick, V. T. Woods, I. T. Ferguson, A. Hoffmann, A.G.U. Perera and N. Dietz, Mat. Res. Soc. Symp. Proc. **955E**; Symposium I: Advances in III-V Nitride Semiconductor Materials and Devices, (ed. C.R. Abernathy, H. Jiang, J.M. Zavada) Boston, MA, USA, Nov.-Dec. 2006, Paper# 0955-I08-04, pp. 1-6 (2007).

III.4 Presentations at conferences/seminars during award period:

Invited Presentation:

7 "Is a common processing window for integrating group III-nitride alloys achievable?" Nikolaus Dietz, Department of Electrical &Computer Engineering, The University of North Carolina at Charlotte, Jan. 14 2010.

6 "Magnetic/Photonic structures based on confined group III-nitride nanocomposites and heterostructures," Nikolaus Dietz, M. Alevli, M. Buegler, G. Durkaya, M. Jamil, and I.T. Ferguson, International Conference on Nanomaterials and Nanosystems" (NanoMats2009) ITU Istanbul, Turkey, 3:00pm, August 11 (2009).

5 "The growth of indium-rich group III-N alloys and heterostructures by high-pressure CVD," N. Dietz, M. Alevli, R. Atalay, M. Buegler, G. Durkaya, E. Malguth, and J. Wang, SPIE - Optics & Photonics, San Diego CA, 2-6 Aug. 2009, Ninth International Conference on Solid State Lighting, Session 10: OLEDs and Solid State Lighting, Paper 7422-12, 11:30am, 4th August (2009).

4 "The characterization of indium-rich InGaN layers grown under high-pressure CVD conditions," Department of Materials Science, Georgia Institute of Technology, Jan. 20, 2009.

3 "The growth and characterization of InN grown by high-pressure CVD," Department Solar Energy, Helmholtz-Zentrum Berlin, May 29, 2008.

2 "The growth and characterization of InN layers grown by high-pressure CVD," Department of Physics, Technical University Berlin, Dec. 17, 2007.

1 "High-pressure chemical vapor deposition: an enabling technology for the fabrication of embedded indium rich $In_{1-x}Ga_xN$ heterostructures," N. Dietz, M. Alevli, G. Durkaya, R. Atalay, W. Fenwick, I. T. Ferguson, in "Seventh International Conference on Solid State Lighting" at the SPIE meeting in San Diego, CA; 27 Aug. 2007. 11am, Paper 6669-19.

Conference - oral contributions

11 "Characterization of high-pressure Chemical Vapor Deposition grown InGaN layers by IR reflectance spectroscopy," I. Senevirathna, M. Buegler, R. Atalay, G. Durkaya, J. Wang, and N. Dietz, 76th Annual Meeting SESAPS, Nov. 12, 2009; 4:15pm, EC.00003, Atlanta, Georgia (2009).

14 "Optical properties of InGaN layers," J. Wang, M. Alevli, R. Atalay, G. Durkaya, M. Buegler, I. Senevirathna, and N. Dietz, 76th Annual Meeting SESAPS, Nov. 12, 2009; 4:00pm, EC.00002, Atlanta, Georgia (2009).

13 "Growth of InN and In rich InGaN by High-Pressure Chemical Vapor Deposition (HPCVD)," M. Buegler, M. Alevli, R. Atalay, G. Durkaya, J. Wang, I. Senevirathna, M. Jamil, I. Ferguson, and N. Dietz, 76th Annual Meeting SESAPS, Nov. 12, 2009; 3:45pm, EC.00001, Atlanta, Georgia (2009).

12 "High-pressure CVD: A novel growths technique for embedded InN alloys and nanostructures," M. Alevli, G. Durkaya, R. Atalay, M. Buegler and Nikolaus Dietz, International Conference on Nanomaterials and Nanosystems" (NanoMats2009) ITU Istanbul, Turkey, 3:00pm, August 10 (2009).

11 "Optical and structural properties of $In_{1-x}Ga_xN$ layers grown by HPCVD," M. Buegler, G. Durkaya, E. Malguth, W.E. Fenwick, I.T. Ferguson, and N. Dietz, SPIE - Optics & Photonics, San Diego CA, 2-6 Aug. 2009, Ninth International Conference on Solid State Lighting, Session 7: Growth III, Paper 7422-23, 8:15-10:05am, 5th August (2009).

10 "The growth and characterization of indium-rich InGaN alloys and heterostructures by high-pressure CVD," N. Dietz, M. Alevli, R. Atalay, M. Buegler, G. Durkaya, E. Malguth, and I.T. Ferguson, E-MRS June 8-12, 2009, Strasbourg, France, Symposium J - Group III nitride semiconductors, 11:15am, June 09 (2009).

9 "Electron accumulation on bare and hydrogenated indium nitride surfaces," B. Thoms, R. Bhatta, A. Acharya, M. Alevli, and N. Dietz, 2009 APS March Meeting, Session Y12: Electronic and Lattice Properties, Including Quantum Size Effects, Abstract Y12.00015, Pittsburgh, Pennsylvania, March 20 (2009).

8 "The characterization of InN properties grown by high-pressure CVD," N. Dietz, M. Alevli, R. Atalay, M. Buegler, G. Durkaya, R. Collazo, J. Tweedie, S. Mita and Z. Sitar, 14th International Conference of Metalorganic Vapor Phase Epitaxy: IC-ICMOVPE-XIV, METZ, France; We-A1.1, 10am, June 04 (2008).

7 "Raman analysis and luminescence properties of InN layers grown by high pressure CVD," R. Kirste, J.-H. Schulze, M.R. Wagner, M. Alevli, A. Hoffmann, and N. Dietz, 7th International Symposium on Semiconductor Light Emitting Devices, April 27 - May 2, Phoenix, Arizona (2008).

6 "Effect of hydrogen on surface electron accumulation in InN films," R. Bhatta, B. Thoms, M. Alevli, and N. Dietz, 2008 APS March Meeting Session D37: Optical Properties of Semiconductors, March 10, 2008, New Orleans, Louisiana (2008).

5 "Optical properties of InN layers grown by high pressure CVD," R. Kirste, M. Alevli, M. R. Wagner, N. Dietz, and A. Hoffmann; 72. Annual Meeting of the DPG and DPG Spring Meeting of the Condensed Matter Division, Berlin, February 25-29, 2008.

4 "Optical Characterezation of InN layers grown by High-Pressure CVD," M. Alevli, G. Durkaya, R. Kirste, A. Weesekara, A.G.U. Perera, A. Hoffmann, and N. Dietz; AVS 54th Intern. Symp.; Oct. 14-19, 2007; Seattle, WA (Session TF1-ThA10, Thursday Oct. 18, 5 pm).

3 "Desorption of Hydrogen from the Indium Nitride Surface Studied by HREELS," R.P. Bhatta, B.D. Thoms, M. Alevli, and N. Dietz; AVS 54th Intern. Symp.; Oct. 14-19, 2007; Seattle, WA (Session SS2-ThM2, Thursday Oct. 18, 8:20 am).

2 "Structural and Surface-Morphological Analysis of InN Layers Grown by HPCVD," G. Durkaya, M. Alevli, R. Atalay, W. Fenwick, I. Ferguson, and N. Dietz; AVS 54th Intern. Symp.; Oct. 14-19, 2007; Seattle, WA (Session SS2-ThM1, Thursday Oct. 18, 8 am).

1 "The Growth and Characterization of InN Layers Grown by High pressure CVD," Nikolaus Dietz; Mustafa Alevli; Ramazan Atalay; Goksel Durkaya; William Fenwick; Hun Kang; and Ian Ferguson; at 7th Int'l Conference on Nitride Semiconductors (ICNS-7) Sept 16-21, 2007, LasVegas, Nevada (Thursday, September 20, 2007 10:15 am)

Conference - poster contributions

14 "The Characterization of Indium-rich InGaN Alloys Grown by High-pressure CVD," N. Dietz, M. Alevli, R. Atalay, M. Buegler, G. Durkaya, R. Kirste, J.-H. Schulze and A. Hoffmann, paper I5.21; in "II-Nitride Growth, Doping, and Device Processing," December 1, 2009 8:00pm, MRS Fall meeting, Boston MA Nov. 30 - Dec. 04 (2009).

13 "Structural studies on the phase stability of $In_{1-x}Ga_xN$ layers," G. Durkaya, R. Atalay, M. Buegler, M. Alevli, M. Jamil, I. Ferguson, and N. Dietz, 76th Annual Meeting SESAPS, LA.00014, Nov. 13, 2009; Atlanta, Georgia (2009).

12 "Composition and Structure of HPCVD-grown InGaN", A. Acharya, M. Buegler, G. Durkaya, B. Thoms, and N. Dietz, 76th Annual Meeting SESAPS, LA.00017, Nov. 13, 2009; Atlanta, Georgia (2009).

11 "Optical Properties of Indium-Rich InGaN Alloys Grown by HPCVD," M. Buegler, R. Atalay, G. Durkaya, E. Malguth, J. Wang, O. Hitzemann, M. Kaiser, R. Kirste, A. Hoffmann, N. Dietz, paper MP156, 5:45pm-19:45pm, Oct. 19, 2009 at 8th International Conference on Nitride Semiconductors (ICNS-8), ICC Jeju, Jeju, Korea, October 18-23 (2009).

10 "Optical and structural properties of InN grown by HPCVD," M. Alevli, M. Buegler, G. Durkaya, E. Malguth, J. Wang, I.T. Ferguson, and N. Dietz, SPIE - Optics & Photonics, San Diego CA, 2-6 Aug. 2009, Ninth International Conference on Solid State Lighting, Poster Session, Paper 7422-42, 8-10am, 4^{th} August (2009).

9 "Optical and structural analysis of $In_{1-x}Ga_xN$ layers grown by HPCVD," M. Buegler, G. Durkaya, E. Malguth, J. Wang, W. Fenwick, I. Ferguson, and N. Dietz, E-MRS June 8 - 12, 2009, Strasbourg, France, Symposium J - Group III nitride semiconductors, June 10 (2009).

8 "Growth and characterization of InN and indium-rich $In_{1-x}Ga_xN$ by high-pressure CVD," Nikolaus Dietz, M. Alevli, R. Atalay, M. Buegler, G. Durkaya, E. Malguth, J. Wang, W. Fenwick, M. Jamil, and I. Ferguson, Air Force Office of Scientific Research, Joint Electronics Program Review, 27-29 May 2009, Arlington, VA 22203 (2009).

7 "Optical and structural analysis of $In_{1-x}Ga_xN$ alloys grown by HPCVD," G. Durkaya, M. Buegler, E. Malguth, W. Fenwick, I. Ferguson, and N. Dietz, 2009 MRS Spring Meeting, San Francisco, CA, April 14-16, 2009, Abstract ID# M8.11, Symposium M: Thin-Film Compound Semiconductor Photovoltaics, April 16 (2009).

6 "Optical and structural analysis of $In_{1-x}Ga_xN$ alloys grown by HPCVD," G. Durkaya, M. Buegler, E. Malguth, W. Fenwick, I. Ferguson and N. Dietz, 2009 APS March Meeting, Session K1, Abstract: K1.00206, Pittsburgh, Pennsylvania, March 20 (2009).

5 “Role of Adsorbates in Surface Electron Accumulation on InN Films,” R. P. Bhatta, A. R. Acharya, B. D. Thoms, M. Alevli, and N. Dietz, AVS 55th International Symposium, Boston, MA, Oct. 19-24, 2008.

4 “The growth of InN and indium-rich InGaN alloys by high-pressure CVD,” M. Buegler, R. Atalay, J.-H. Schulze, R. Collazo, Z. Sitar, A. Hoffmann, and N. Dietz, Mo2a-P12, at IWN2008, Montreux, Switzerland, Oct. 6-12, 2008.

3 “Optical Properties of InN Grown on Templates with Controlled Surface Polarities,” R. Kirste, M. Buegler, J.-H. Schulze, N. Dietz, and A. Hoffmann, Mo2a-P3 at IWN2008, Montreux, Switzerland, Oct. 6-12, 2008.

2 "Structure of Isolated Oxygen Impurity States in InN," D. Alexandrov; S. Butcher, and N. Dietz; MRS Symp. Q: Nitrides and Related Bulk Materials; Nov. 25-30, 2007; Boston, MA (Session Q9.15, Thu, Nov 29, 8 - 11 pm).

1 "Micro-Raman Analysis on InN Layers Grown by HPCVD," Ronny Kirste; Mustafa Alevli; Nikolaus Dietz; and Axel Hoffmann; at 7th Int'l Conference on Nitride Semiconductors (ICNS-7) Sept 16-21, 2007, LasVegas, Nevada (Wednesday, September 19, 2007 (1:30-2:30 pm).